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# 4-(4-Bromophenyl)-4,5,6,7-tetrahydro-3-methyl-6-oxo-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitrile ethanol solvate

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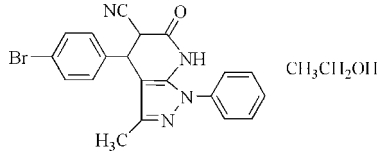
Key indicators: single-crystal X-ray study; $T$ = 295 K; mean $\sigma$(C–C) = 0.005 Å; $R$ factor = 0.047; $wR$ factor = 0.122; data-to-parameter ratio = 14.9.

In the structure of the title compound, $C_{20}H_{15}BrN_4O\cdot C_2H_6O$, the hydrogenated pyridinone ring adopts an envelope conformation. The dihedral angle between the bromo-substituted phenyl ring and the pyrazole ring is 79.6 (1)°, and that between the non-substituted phenyl ring and the pyrazole ring is 51.2 (1)°. In the crystal structure, molecules are linked *via* intermolecular N—H···O and O—H···N hydrogen bonds. A short intermolecular N···Br contact [3.213 (4) Å] is present in the crystal structure.

## Related literature

For general background, see: Falcó *et al.* (2005); Kung & Wager (2007).




## Experimental

### Crystal data

$C_{20}H_{15}BrN_4O\cdot C_2H_6O$ $M_r$ = 453.34
Monoclinic, $P2_1/c$
$a$ = 21.871 (9) Å
$b$ = 9.209 (4) Å
$c$ = 10.552 (5) Å
$\beta$ = 90.370 (5)°
$V$ = 2125.4 (15) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 1.96 mm$^{-1}$
$T$ = 295 (2) K
0.31 × 0.24 × 0.14 mm

### Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{min}$ = 0.586, $T_{max}$ = 0.770
10428 measured reflections
3947 independent reflections
2414 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.035

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.121
$S$ = 1.01
3947 reflections
265 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.53 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.51 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O2—H2···N1$^{i}$ | 0.82 | 2.06 | 2.874 (4) | 171 |
| N3—H3$D$···O2 | 0.97 | 1.84 | 2.786 (3) | 166 |

Symmetry code: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2452).

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# supplementary materials

*Acta Cryst.* (2008). E**64**, o1925 [ **doi:10.1107/S1600536808028638** ]

# 4-(4-Bromophenyl)-4,5,6,7-tetrahydro-3-methyl-6-oxo-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine-5-carbonitrile ethanol solvate

**X.-S. Fan, X.-Y. Li, X. Wang, D.-F. Li and X.-Y. Zhang**

## Comment

Pyrazolo[3,4-*b*]pyridine-6-ones as a subunit of pyrazolo[3,4-*b*]pyridine acted as potential hypnotic drugs in many cases (Falcó *et al.*, 2005). Hydrogenated pyrazolo[3,4-*b*]pyridin-6-ones have been found with good biological activity such as GSK-3 inhibitors (Kung *et al.*, 2007) and have the potential to be used as novel building blocks to construct new nitrogen-containing molecules. The title compound is one of the hydrogenated pyrazolo[3,4-*b*]pyridin-6-one derivatives. Its crystal structure is presented here.

In the title compound (Fig. 1) there are four rings, three planar rings and one nonplanar hydrogenated pyridinone ring. The hydrogenated pyridinone ring is fused to the pyrazole ring and adopts an envelope conformation with C4 at flap position. The dihedral angle between the bromo-substituted benzene ring and the pyrazole ring is 79.6 (1)° and that between the non-substituted phenyl ring and the pyrazole ring is 51.2 (1)°.

Intermolecular N—H···O and O—H···N hydrogen bonding (Table 1) and the weak intermolecular Br1···N4$^{i}$ contact present in the crystal structure [symmetry code: (i) 1-x, -1/2+y, 1/2-z].

## Experimental

4-Bromobenzaldehyde (1 mmol) and ethyl cyanoacetate (1 mmol) were added to 1 ml of 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][$BF_4$]). The mixture was stirred at 353 K until the disappearance of bromobenzaldehyde. Upon cooling to room temperature, 5-amino-3-methyl-1-phenylpyrazole (1 mmol) was added and the mixture was stirred at room temperature for a certain period of time to complete the reaction (monitored by TLC). The reaction time was 9 h totally. Upon completion, the product was not separated from the reaction system; instead, 4 ml of ethanol was added. Single crystals of the title compound were obtained by slow evaporation of the solvent.

## Refinement

H-atoms were included in calculated positions and treated as riding atoms: N—H = 0.97 Å, O—H = 0.82 Å and C—H = 0.93–0.98 Å with $U_{iso}$(H) = 1.5$U_{eq}$($CH_3$, OH, NH) and 1.2$U_{eq}$(CH, $CH_2$).

## Figures

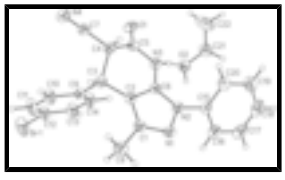


Fig. 1. Molecular structure of the title compound with displacement ellipsoids drawn at the 30% probability level. Dashed line indicates hydrogen bonding.

**4-(4-Bromophenyl)-4,5,6,7-tetrahydro-3-methyl-6-oxo-1-phenyl-1*H*- pyrazolo[3,4-*b*]pyridine-5-carbonitrile ethanol solvate**

*Crystal data*

| | |
|---|---|
| $C_{20}H_{15}BrN_4O\cdot C_2H_6O$ | $F_{000}$ = 928 |
| $M_r$ = 453.34 | $D_x$ = 1.417 Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation<br>λ = 0.71073 Å |
| Hall symbol: -P 2ybc | Cell parameters from 2154 reflections |
| $a$ = 21.871 (9) Å | θ = 2.4–22.3º |
| $b$ = 9.209 (4) Å | μ = 1.96 mm$^{-1}$ |
| $c$ = 10.552 (5) Å | $T$ = 295 (2) K |
| β = 90.370 (5)º | Block, colourless |
| $V$ = 2125.4 (15) Å$^3$ | 0.31 × 0.24 × 0.14 mm |
| $Z$ = 4 | |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 3947 independent reflections |
| Radiation source: fine-focus sealed tube | 2414 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int}$ = 0.035 |
| $T$ = 295(2) K | $\theta_{max}$ = 25.5º |
| φ and ω scans | $\theta_{min}$ = 2.4º |
| Absorption correction: multi-scan (SADABS; Bruker, 1997) | $h$ = −26→26 |
| $T_{min}$ = 0.586, $T_{max}$ = 0.770 | $k$ = −11→9 |
| 10428 measured reflections | $l$ = −12→12 |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)]$ = 0.046 | H-atom parameters constrained |
| $wR(F^2)$ = 0.121 | $w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 1.3425P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S$ = 1.01 | $(\Delta/\sigma)_{max}$ = 0.001 |
| 3947 reflections | $\Delta\rho_{max}$ = 0.53 e Å$^{-3}$ |
| 265 parameters | $\Delta\rho_{min}$ = −0.51 e Å$^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none |

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on $F^2$, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on $F^2$ are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Br1 | 0.449857 (19) | 0.58567 (7) | 0.18723 (5) | 0.1023 (3) |
| O1 | 0.77687 (11) | 0.8095 (2) | 0.2363 (2) | 0.0553 (6) |
| O2 | 0.83439 (11) | 0.5202 (3) | 0.0508 (2) | 0.0558 (6) |
| H2 | 0.8220 | 0.4430 | 0.0218 | 0.084* |
| N1 | 0.77906 (13) | 0.2474 (3) | 0.4696 (2) | 0.0478 (7) |
| N2 | 0.80852 (12) | 0.3344 (3) | 0.3832 (2) | 0.0431 (6) |
| N3 | 0.79796 (12) | 0.5800 (3) | 0.2978 (2) | 0.0434 (6) |
| H3D | 0.8174 | 0.5606 | 0.2174 | 0.065* |
| N4 | 0.67632 (15) | 0.9759 (4) | 0.4375 (3) | 0.0732 (9) |
| C1 | 0.73512 (15) | 0.3303 (4) | 0.5195 (3) | 0.0442 (8) |
| C2 | 0.73547 (14) | 0.4703 (3) | 0.4646 (3) | 0.0404 (7) |
| C3 | 0.69597 (14) | 0.6023 (3) | 0.4808 (3) | 0.0414 (8) |
| H3 | 0.6870 | 0.6128 | 0.5712 | 0.050* |
| C4 | 0.73741 (14) | 0.7328 (3) | 0.4401 (3) | 0.0407 (8) |
| H4 | 0.7688 | 0.7432 | 0.5061 | 0.049* |
| C5 | 0.77157 (14) | 0.7129 (4) | 0.3138 (3) | 0.0418 (8) |
| C6 | 0.78163 (14) | 0.4672 (3) | 0.3795 (3) | 0.0387 (7) |
| C7 | 0.70350 (16) | 0.8703 (4) | 0.4370 (3) | 0.0487 (8) |
| C8 | 0.69393 (18) | 0.2752 (4) | 0.6197 (3) | 0.0648 (10) |
| H8A | 0.6546 | 0.2537 | 0.5833 | 0.097* |
| H8B | 0.6895 | 0.3477 | 0.6843 | 0.097* |
| H8C | 0.7110 | 0.1886 | 0.6561 | 0.097* |
| C9 | 0.63578 (14) | 0.5971 (3) | 0.4089 (3) | 0.0426 (8) |
| C10 | 0.58214 (16) | 0.6426 (4) | 0.4648 (3) | 0.0628 (10) |
| H10 | 0.5830 | 0.6750 | 0.5482 | 0.075* |
| C11 | 0.52737 (17) | 0.6412 (5) | 0.3997 (4) | 0.0771 (13) |
| H11 | 0.4918 | 0.6721 | 0.4391 | 0.092* |
| C12 | 0.52561 (16) | 0.5939 (4) | 0.2764 (4) | 0.0626 (10) |
| C13 | 0.57776 (16) | 0.5502 (4) | 0.2179 (3) | 0.0661 (11) |
| H13 | 0.5765 | 0.5189 | 0.1341 | 0.079* |
| C14 | 0.63241 (16) | 0.5528 (4) | 0.2835 (3) | 0.0586 (10) |
| H14 | 0.6680 | 0.5240 | 0.2427 | 0.070* |
| C15 | 0.85626 (15) | 0.2756 (4) | 0.3081 (3) | 0.0456 (8) |

| | | | | |
|---|---|---|---|---|
| C16 | 0.84675 (18) | 0.1459 (4) | 0.2460 (3) | 0.0559 (9) |
| H16 | 0.8097 | 0.0969 | 0.2529 | 0.067* |
| C17 | 0.8936 (2) | 0.0902 (5) | 0.1732 (4) | 0.0769 (13) |
| H17 | 0.8880 | 0.0026 | 0.1309 | 0.092* |
| C18 | 0.9477 (2) | 0.1616 (6) | 0.1624 (4) | 0.0854 (14) |
| H18 | 0.9786 | 0.1231 | 0.1125 | 0.103* |
| C19 | 0.95680 (19) | 0.2899 (6) | 0.2249 (4) | 0.0816 (13) |
| H19 | 0.9939 | 0.3384 | 0.2175 | 0.098* |
| C20 | 0.91114 (17) | 0.3477 (4) | 0.2990 (4) | 0.0627 (10) |
| H20 | 0.9174 | 0.4344 | 0.3423 | 0.075* |
| C21 | 0.89214 (19) | 0.5522 (5) | −0.0008 (4) | 0.0750 (12) |
| H21A | 0.8879 | 0.5692 | −0.0911 | 0.090* |
| H21B | 0.9192 | 0.4699 | 0.0114 | 0.090* |
| C22 | 0.9183 (3) | 0.6785 (6) | 0.0587 (6) | 0.128 (2) |
| H22A | 0.8972 | 0.7637 | 0.0298 | 0.192* |
| H22B | 0.9607 | 0.6855 | 0.0371 | 0.192* |
| H22C | 0.9144 | 0.6704 | 0.1490 | 0.192* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.0484 (3) | 0.1630 (6) | 0.0952 (4) | 0.0022 (3) | −0.0134 (2) | −0.0219 (3) |
| O1 | 0.0811 (17) | 0.0401 (14) | 0.0446 (13) | −0.0010 (13) | 0.0004 (11) | 0.0073 (11) |
| O2 | 0.0628 (16) | 0.0541 (16) | 0.0508 (13) | −0.0062 (13) | 0.0098 (11) | −0.0147 (12) |
| N1 | 0.0548 (17) | 0.0385 (16) | 0.0503 (16) | −0.0019 (14) | 0.0086 (13) | 0.0083 (13) |
| N2 | 0.0485 (16) | 0.0365 (16) | 0.0444 (14) | 0.0022 (14) | 0.0089 (12) | 0.0029 (13) |
| N3 | 0.0540 (16) | 0.0375 (16) | 0.0387 (14) | 0.0027 (13) | 0.0093 (12) | 0.0032 (12) |
| N4 | 0.065 (2) | 0.049 (2) | 0.105 (3) | 0.0064 (18) | −0.0053 (18) | −0.0055 (19) |
| C1 | 0.0478 (19) | 0.039 (2) | 0.0458 (18) | −0.0049 (17) | 0.0068 (15) | 0.0041 (16) |
| C2 | 0.0456 (18) | 0.039 (2) | 0.0366 (16) | 0.0001 (16) | 0.0007 (14) | 0.0015 (14) |
| C3 | 0.0476 (18) | 0.042 (2) | 0.0344 (15) | −0.0009 (16) | 0.0043 (13) | −0.0030 (14) |
| C4 | 0.0491 (18) | 0.0367 (19) | 0.0364 (16) | 0.0024 (16) | −0.0051 (14) | −0.0046 (14) |
| C5 | 0.0486 (19) | 0.040 (2) | 0.0371 (16) | −0.0037 (16) | −0.0039 (14) | 0.0000 (16) |
| C6 | 0.0447 (18) | 0.0332 (19) | 0.0383 (16) | 0.0012 (15) | 0.0017 (14) | 0.0015 (14) |
| C7 | 0.052 (2) | 0.040 (2) | 0.054 (2) | −0.0029 (18) | −0.0030 (16) | −0.0052 (16) |
| C8 | 0.074 (3) | 0.053 (2) | 0.068 (2) | −0.001 (2) | 0.024 (2) | 0.0119 (19) |
| C9 | 0.0445 (18) | 0.0367 (19) | 0.0466 (18) | 0.0004 (15) | 0.0051 (14) | −0.0050 (15) |
| C10 | 0.055 (2) | 0.084 (3) | 0.049 (2) | −0.001 (2) | 0.0105 (17) | −0.0201 (19) |
| C11 | 0.043 (2) | 0.117 (4) | 0.072 (3) | 0.004 (2) | 0.0126 (19) | −0.022 (3) |
| C12 | 0.043 (2) | 0.075 (3) | 0.069 (2) | −0.001 (2) | −0.0050 (18) | −0.009 (2) |
| C13 | 0.054 (2) | 0.087 (3) | 0.057 (2) | 0.005 (2) | −0.0018 (18) | −0.025 (2) |
| C14 | 0.047 (2) | 0.073 (3) | 0.056 (2) | 0.0102 (19) | 0.0020 (16) | −0.0236 (19) |
| C15 | 0.050 (2) | 0.043 (2) | 0.0433 (17) | 0.0105 (17) | 0.0019 (15) | 0.0024 (16) |
| C16 | 0.071 (2) | 0.046 (2) | 0.051 (2) | 0.0061 (19) | 0.0051 (18) | −0.0011 (17) |
| C17 | 0.119 (4) | 0.052 (3) | 0.060 (2) | 0.021 (3) | 0.017 (2) | −0.004 (2) |
| C18 | 0.091 (4) | 0.086 (4) | 0.080 (3) | 0.038 (3) | 0.034 (3) | 0.012 (3) |
| C19 | 0.054 (3) | 0.093 (4) | 0.098 (3) | 0.008 (3) | 0.017 (2) | 0.007 (3) |
| C20 | 0.054 (2) | 0.062 (3) | 0.072 (2) | 0.002 (2) | 0.0058 (19) | −0.001 (2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C21 | 0.071 (3) | 0.079 (3) | 0.075 (3) | −0.010 (2) | 0.016 (2) | −0.015 (2) |
| C22 | 0.105 (4) | 0.127 (5) | 0.152 (5) | −0.062 (4) | 0.036 (4) | −0.049 (4) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Br1—C12 | 1.901 (4) | C9—C14 | 1.386 (4) |
| O1—C5 | 1.215 (3) | C10—C11 | 1.377 (5) |
| O2—C21 | 1.409 (4) | C10—H10 | 0.9300 |
| O2—H2 | 0.8200 | C11—C12 | 1.373 (5) |
| N1—C1 | 1.338 (4) | C11—H11 | 0.9300 |
| N1—N2 | 1.377 (3) | C12—C13 | 1.361 (5) |
| N2—C6 | 1.357 (4) | C13—C14 | 1.378 (5) |
| N2—C15 | 1.422 (4) | C13—H13 | 0.9300 |
| N3—C5 | 1.364 (4) | C14—H14 | 0.9300 |
| N3—C6 | 1.398 (4) | C15—C20 | 1.376 (5) |
| N3—H3D | 0.9687 | C15—C16 | 1.377 (5) |
| N4—C7 | 1.140 (4) | C16—C17 | 1.383 (5) |
| C1—C2 | 1.414 (4) | C16—H16 | 0.9300 |
| C1—C8 | 1.482 (4) | C17—C18 | 1.359 (6) |
| C2—C6 | 1.356 (4) | C17—H17 | 0.9300 |
| C2—C3 | 1.502 (4) | C18—C19 | 1.367 (6) |
| C3—C9 | 1.516 (4) | C18—H18 | 0.9300 |
| C3—C4 | 1.567 (4) | C19—C20 | 1.379 (5) |
| C3—H3 | 0.9800 | C19—H19 | 0.9300 |
| C4—C7 | 1.468 (5) | C20—H20 | 0.9300 |
| C4—C5 | 1.544 (4) | C21—C22 | 1.438 (6) |
| C4—H4 | 0.9800 | C21—H21A | 0.9700 |
| C8—H8A | 0.9600 | C21—H21B | 0.9700 |
| C8—H8B | 0.9600 | C22—H22A | 0.9600 |
| C8—H8C | 0.9600 | C22—H22B | 0.9600 |
| C9—C10 | 1.381 (5) | C22—H22C | 0.9600 |
| C21—O2—H2 | 109.5 | C9—C10—H10 | 119.2 |
| C1—N1—N2 | 105.7 (2) | C12—C11—C10 | 119.6 (3) |
| C6—N2—N1 | 109.8 (2) | C12—C11—H11 | 120.2 |
| C6—N2—C15 | 130.3 (3) | C10—C11—H11 | 120.2 |
| N1—N2—C15 | 119.7 (3) | C13—C12—C11 | 120.4 (3) |
| C5—N3—C6 | 118.8 (3) | C13—C12—Br1 | 119.6 (3) |
| C5—N3—H3D | 117.5 | C11—C12—Br1 | 120.0 (3) |
| C6—N3—H3D | 121.2 | C12—C13—C14 | 119.6 (3) |
| N1—C1—C2 | 110.6 (3) | C12—C13—H13 | 120.2 |
| N1—C1—C8 | 121.8 (3) | C14—C13—H13 | 120.2 |
| C2—C1—C8 | 127.5 (3) | C13—C14—C9 | 121.7 (3) |
| C6—C2—C1 | 105.0 (3) | C13—C14—H14 | 119.1 |
| C6—C2—C3 | 121.6 (3) | C9—C14—H14 | 119.1 |
| C1—C2—C3 | 133.4 (3) | C20—C15—C16 | 121.0 (3) |
| C2—C3—C9 | 114.6 (3) | C20—C15—N2 | 120.0 (3) |
| C2—C3—C4 | 104.8 (2) | C16—C15—N2 | 119.1 (3) |
| C9—C3—C4 | 112.9 (2) | C15—C16—C17 | 118.4 (4) |
| C2—C3—H3 | 108.1 | C15—C16—H16 | 120.8 |

| | | | |
|---|---|---|---|
| C9—C3—H3 | 108.1 | C17—C16—H16 | 120.8 |
| C4—C3—H3 | 108.1 | C18—C17—C16 | 121.0 (4) |
| C7—C4—C5 | 109.3 (3) | C18—C17—H17 | 119.5 |
| C7—C4—C3 | 112.0 (3) | C16—C17—H17 | 119.5 |
| C5—C4—C3 | 115.4 (2) | C17—C18—C19 | 120.1 (4) |
| C7—C4—H4 | 106.5 | C17—C18—H18 | 119.9 |
| C5—C4—H4 | 106.5 | C19—C18—H18 | 119.9 |
| C3—C4—H4 | 106.5 | C18—C19—C20 | 120.2 (4) |
| O1—C5—N3 | 122.1 (3) | C18—C19—H19 | 119.9 |
| O1—C5—C4 | 122.9 (3) | C20—C19—H19 | 119.9 |
| N3—C5—C4 | 114.9 (3) | C15—C20—C19 | 119.3 (4) |
| C2—C6—N2 | 108.9 (3) | C15—C20—H20 | 120.4 |
| C2—C6—N3 | 125.9 (3) | C19—C20—H20 | 120.4 |
| N2—C6—N3 | 125.1 (3) | O2—C21—C22 | 110.8 (3) |
| N4—C7—C4 | 178.1 (4) | O2—C21—H21A | 109.5 |
| C1—C8—H8A | 109.5 | C22—C21—H21A | 109.5 |
| C1—C8—H8B | 109.5 | O2—C21—H21B | 109.5 |
| H8A—C8—H8B | 109.5 | C22—C21—H21B | 109.5 |
| C1—C8—H8C | 109.5 | H21A—C21—H21B | 108.1 |
| H8A—C8—H8C | 109.5 | C21—C22—H22A | 109.5 |
| H8B—C8—H8C | 109.5 | C21—C22—H22B | 109.5 |
| C10—C9—C14 | 117.1 (3) | H22A—C22—H22B | 109.5 |
| C10—C9—C3 | 121.0 (3) | C21—C22—H22C | 109.5 |
| C14—C9—C3 | 121.8 (3) | H22A—C22—H22C | 109.5 |
| C11—C10—C9 | 121.6 (3) | H22B—C22—H22C | 109.5 |
| C11—C10—H10 | 119.2 | | |
| C1—N1—N2—C6 | −1.3 (3) | C5—N3—C6—C2 | 9.3 (4) |
| C1—N1—N2—C15 | −176.8 (3) | C5—N3—C6—N2 | −172.9 (3) |
| N2—N1—C1—C2 | 0.7 (3) | C5—C4—C7—N4 | 168 (11) |
| N2—N1—C1—C8 | −178.6 (3) | C3—C4—C7—N4 | 39 (12) |
| N1—C1—C2—C6 | 0.0 (3) | C2—C3—C9—C10 | 137.1 (3) |
| C8—C1—C2—C6 | 179.4 (3) | C4—C3—C9—C10 | −103.1 (4) |
| N1—C1—C2—C3 | 177.5 (3) | C2—C3—C9—C14 | −45.7 (4) |
| C8—C1—C2—C3 | −3.1 (6) | C4—C3—C9—C14 | 74.2 (4) |
| C6—C2—C3—C9 | 97.3 (3) | C14—C9—C10—C11 | 1.3 (6) |
| C1—C2—C3—C9 | −79.9 (4) | C3—C9—C10—C11 | 178.7 (4) |
| C6—C2—C3—C4 | −27.0 (4) | C9—C10—C11—C12 | −0.1 (7) |
| C1—C2—C3—C4 | 155.8 (3) | C10—C11—C12—C13 | −0.8 (7) |
| C2—C3—C4—C7 | 173.7 (2) | C10—C11—C12—Br1 | 178.0 (3) |
| C9—C3—C4—C7 | 48.4 (3) | C11—C12—C13—C14 | 0.5 (6) |
| C2—C3—C4—C5 | 47.8 (3) | Br1—C12—C13—C14 | −178.4 (3) |
| C9—C3—C4—C5 | −77.5 (3) | C12—C13—C14—C9 | 0.8 (6) |
| C6—N3—C5—O1 | −169.4 (3) | C10—C9—C14—C13 | −1.7 (6) |
| C6—N3—C5—C4 | 13.4 (4) | C3—C9—C14—C13 | −179.0 (3) |
| C7—C4—C5—O1 | 11.5 (4) | C6—N2—C15—C20 | 54.7 (5) |
| C3—C4—C5—O1 | 138.8 (3) | N1—N2—C15—C20 | −130.8 (3) |
| C7—C4—C5—N3 | −171.3 (3) | C6—N2—C15—C16 | −125.7 (4) |
| C3—C4—C5—N3 | −44.0 (4) | N1—N2—C15—C16 | 48.7 (4) |
| C1—C2—C6—N2 | −0.8 (3) | C20—C15—C16—C17 | −0.6 (5) |

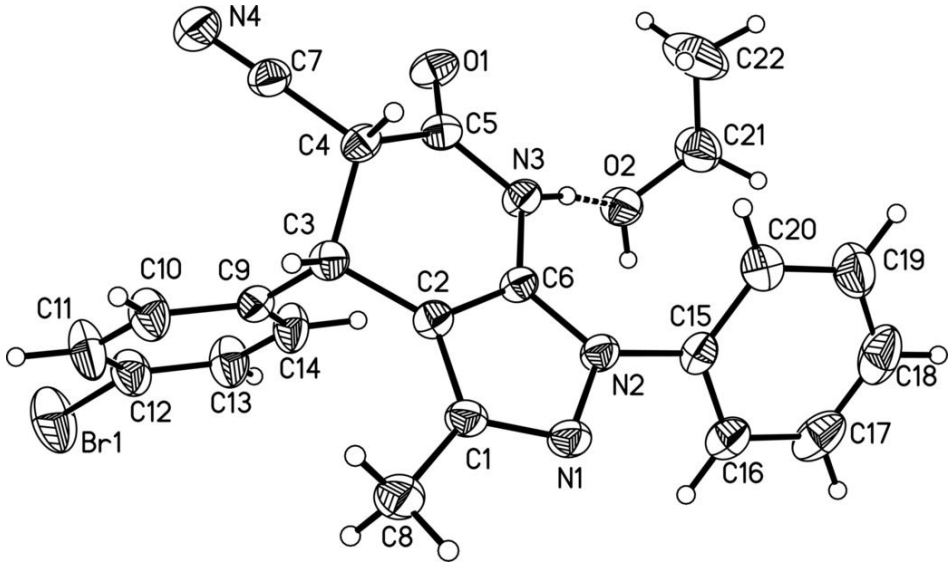
| | | | |
|---|---|---|---|
| C3—C2—C6—N2 | −178.7 (3) | N2—C15—C16—C17 | 179.9 (3) |
| C1—C2—C6—N3 | 177.2 (3) | C15—C16—C17—C18 | −0.2 (6) |
| C3—C2—C6—N3 | −0.6 (5) | C16—C17—C18—C19 | 0.6 (7) |
| N1—N2—C6—C2 | 1.3 (3) | C17—C18—C19—C20 | −0.1 (7) |
| C15—N2—C6—C2 | 176.2 (3) | C16—C15—C20—C19 | 1.0 (5) |
| N1—N2—C6—N3 | −176.7 (3) | N2—C15—C20—C19 | −179.5 (3) |
| C15—N2—C6—N3 | −1.8 (5) | C18—C19—C20—C15 | −0.7 (6) |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O2—H2···N1$^{i}$ | 0.82 | 2.06 | 2.874 (4) | 171 |
| N3—H3D···O2 | 0.97 | 1.84 | 2.786 (3) | 166 |

Symmetry codes: (i) *x*, −*y*+1/2, *z*−1/2.

**Fig. 1**


N4
C7
O1
C22
C5
C4
N3
O2
C21
C3
C20
C19
C10
C9
C2
C6
C11
C15
C14
C18
N2
C12
C13
Br1
C1
N1
C17
C16
C8